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Reversed-Phase Separation of a Standard PAH Mixture
on an Adamantyl Surface

by

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) Reversed-Phase High Performance Liquid Chromatography (HPLC) is an important technique for the analysis of polycyclic aromatic hydrocarbons (PAH). In carrying out the chromatographic separations, octadecyl (C ₁₈) phases often are used because of their excellent selectivity towards PAH. Recently, Sander and Wise have studied and attempted to classify the various parameters which influence solute retention for this class of compounds. Surface coverage and solute shape have been found to be major factors which influence retention behavior. The elution order for polycyclic aromatic hydrocarbons which differ in planarity may reverse depending on structural differences in the C ₁₈ phase being used. As a result of their studies, Sander and Wise have proposed that selected PHAS solutes (e.g., benzo[a]pyrene - BaP, phenanthro[3,4-c]phenanthrene-PhPh, and 1,2:3,4:5,6:7,8-tetrabenzonaphthalene - TBN.) can be used to classify phases in terms of their selectivity. (continued on reverse ->)			
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Reversed-Phase Separation of a Standard PAH mixture
on an Adamantyl Surface

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INTRODUCTION

Reversed phase high performance liquid chromatography (HPLC) is an important technique for the analysis of polycyclic aromatic hydrocarbons (PAH). In carrying out the chromatographic separations, octadecyl (C_{18}) phases often are used because of their excellent selectivity towards PAH. Recently, Sander and Wise have studied and attempted to classify the various parameters (1,2) which influence solute retention for this class of compounds. Surface coverage and solute shape have been found to be major factors which influence retention behavior. The elution order for polycyclic aromatic hydrocarbons which differ in planarity may reverse depending on structural differences in the C_{18} phase being used. As a result of their studies, Sander and Wise have proposed that selected PAH solutes (e.g., benzo[a]pyrene - BaP, phenanthro[3,4-c]phenanthrene - PhPh, and 1,2:3,4:5,6:7,8-tetrabenzonaphthalene - TEN.) can be used to classify phases in terms of their selectivity.

Recently we have reported an unique stationary phase synthesized by exhaustively modifying porous silica with bulky rigid molecules of adamantane. This surface has been shown to produce good peak shapes for basic solutes even under less than favorable chromatographic conditions (3). In the current work the selectivity of the adamantyl surface has been studied. In carrying out the evaluation, the polycyclic

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aromatic hydrocarbon mixture recommended by Sander and Wise
has been used.

EXPERIMENTAL SECTION

Reagent: Adamantylethyltrichlorosilane was purchased from Petrarch System Inc. (Levittown, PA) and was used as received. LiChrosorb Sil100 (dp ~ 10 μ m) was obtained from E. Merck (Darmstadt, West Germany). HPLC grade acetonitrile was purchased from Aldrich Chemical Co. (Milwaukee, WI). Water was purified using a Milli-Q water system (Millipore Co., El Paso, TX). A test mixture containing Bap, PhPh, and TBN in acetonitrile was supplied by the National Bureau of Standards (NBS)(Gaithersburg, MD)

Preparation of adamantyl phase: Adamantylethyltrichlorosilane was used to chemically modify silica as previously described (4). Subsequently, this material was packed into a 4.6 mm i.d. X 150 mm stainless steel column using a dynamic packing procedure (5).

Chromatography: Chromatographic experiments were carried out using a LC/9560 ternary gradient liquid chromatograph (IBM Instruments Inc.) equipped with a UV detector. The column was evaluated using a mobile phase of acetonitrile/water (v/v, 85:15) at a flow rate 2 ml/min.

RESULT AND DISCUSSION

A representative separation of the NBS test mixture on the adamantyl phase is shown in figure 1. Capacity factors (k') of each PAH compound and selectivity values (α) are summerized in table 1. For comparison purposes, data obtained from chromatograms, supplied with the test mixture (6) also are listed for several different C_{18} phases.

The elution order of the PAH compounds ($BaP < PhPh < TBN$) is similar to a commercial monomeric C_{18} phase (e.g., Beckman Ultrasphere ODS phase). Likewise, selectivities, $\alpha(TBN/BaP) = 2.10$, $\alpha(PhPh/BaP) = 1.47$, are closest to this same commercial column. However, the k' data are about 1/3 that obtained from the Beckman column.

Presumably based on the above data a number of other solutes may be expected to behave similarly and the adamantyl surface will be applicable to separations now being carried out on C_{18} columns with similar selectivity. In a more general sense, this probably should not hold true based on geometrical considerations and the proposed "slot" model (2) for PAH solutes. Because of its ball-like structure the adamantyl molecule effectively shields unreacted silanols even for small basic solutes such as aniline (3). Since the surface structure is rigid compared to conventional linear n -alkyl phases, it should not only be useful for carrying out

numerous applications but also should provide an important tool for testing interaction/interfacial models.

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Table 1. Comparison of PAH retention & column selectivity

Column*	capacity factor (k')#			selectivity (α)	
	Bap	PhPh	TBN	PhPh/BaP	TBN/BAP
A	1.55	2.28	3.26	1.47	2.10
B	4.94	5.52	9.77	1.12	1.98
C	3.96	3.96	7.20	1.00	1.82
D	5.56	4.42	7.76	0.79	1.40
E	2.48	1.65	2.68	0.67	1.08
F	3.85	1.97	2.86	0.51	0.74
G	5.57	1.49	1.85	0.27	0.33

*. Columns: A = adamnatyl, B = Beckman Ultrasphere ODS,
 C = Whatman Partisphere C₁₈, D = Whatman Partisil ODS-2,
 E = Vydac TP low load custom synthesis, F = Vydac 201TP,
 G = Vydac TP high load custom synthesis.

#. Solutes: BaP = benzo[a]pyrene,
 PhPh = phenanthro[3,4-c]phenanthrene,
 TBN = 1,2:3,4:5,6:7,8-tetrabenzonaphthalene.
 k' data except column A are from ref.(6).

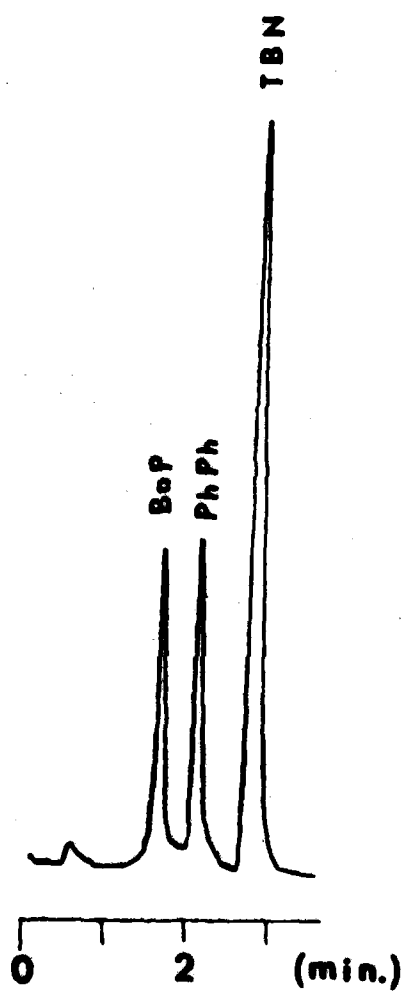
Figure Caption

Figure 1: Chromatogram of the NBS test mixture.

Column: adamantyl (4.6 mm i.d. X 150 mm).

Mobile phase: acetonitrile-water, 85/15, v/v.

Flow rate: 2 ml/min.



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